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A STUDY ON THE DURABILITY OF CONCRETE EXPOSED IN MARINE ENVIRONMENT FOR 20 YEARS

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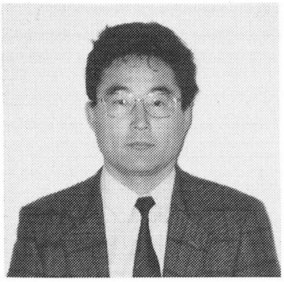

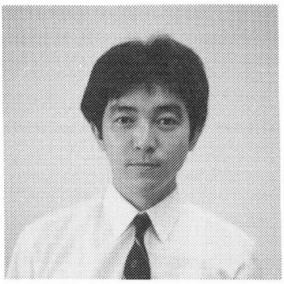

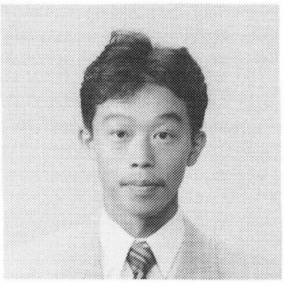

Tsutomu FUKUTE Hidenori HAMADA Kunio YAMAMOTO

SYNOPSIS

In this study, the long-term durability of marine concrete is investigated. This study was started in 1970 at the Port and Harbour Research Institute, Ministry of Transport, Japan. Many specimens with several different factors, such as type of cement, mixing water and cover thickness of reinforcing steel in concrete, were fabricated and exposed under marine environment. During 20 years' exposure, several properties of concrete and reinforcing steel have been tested both chemically and physically. From the test results, several important conclusions were derived. In this paper, some findings from a series of tests are presented.

Keywords: concrete, durability, marine environment, corrosion of reinforcing steel, mixing water

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1. Introduction

Unexpectedly early deterioration of concrete structures which were believed to have semipermanent durability has often been reported; it is becoming a serious social problem. As the main reasons for the early deterioration of concrete structures, the followings are pointed out: the use of insufficiently clean sea sand, the use of an admixture with high salt content, alkali aggregate reactions, insufficient construction control, etc. Therefore, materials for concrete are severely regulated by the Japan Society of Civil Engineers (JSCE), Architectural Institute of Japan, Japanese Industrial Standard (JIS) and so on.

More care is necessary against the corrosion of the reinforcement of concrete structures, such as harbour structures or marine structures which are influenced significantly by salt, than for general land structures[1],[2]. Care is also necessary to prevent deterioration of concrete caused by sulfate contained in seawater. In order to make clear the phenomenon or to confirm the validity of the countermeasures, long-term continuous survey is required, since the corrosion and the deterioration phenomenon progress gradually with time.

As an example of a long-term systematic test on the durability of concrete exposed in marine environments, experiments performed by the Norway Institute of Technology in Trondheim Bay, Norway, since 1936 [3] and by the Corps of Engineers in Treat Island, Maine, U.S.A.[4] are well known. In Japan, when the breakwater in the Port of Otaru, Hokkaido, was constructed in 1896, Dr. Isamu Hiroi made many mortar test specimens; they have been kept in seawater, tap water and air, and the changes in their strength have been surveyed for more than ninety years [5],[6]. Since all of them have been maintained and controlled steadily for a long time, they have offered valuable information to the research field on the durability of concrete.

As for the existing long-term exposure test, since the techniques for investigating the effects of internal and external chloride on the durability of concrete and of the electrochemical characteristics of reinforcement have not been etablished, discussions on these subjects have been very limited.

Based on the above background, in 1970, the Port and Harbour Research Institute (PHRI), Ministry of Transport, Japan, started exposure tests of various concrete test specimens in Kurihama Bay, which can be considered to exhibit typical environmental conditions in Japan. During these twenty years, the effects of type of cement or mixing water on the long-term strength characteristics of concrete, chemical composition of concrete, and the corrosion characteristics of reinforcement have been surveyed. This study is on the physical, chemical and electrochemical considerations of the 20 years' test results. Some parts of the test results up to 5 years were reported in reference [7].

2. Environmental Conditions of the Exposure Site for Specimens

As for the exposure environment, a tidal zone having conditions more serious than those of the submerged zone with respect to concrete deterioration was selected. For the actual exposure, a tidal pool in PHRI, which can simulate tidal movement, was used. The tidal pool is supplied with seawater and drained by a pump twice a day, and the tide movement is simulated with 1.5m of tidal range. The seawater in the tidal pool is pumped up from Kurihama Bay which is contiguous to Tokyo Bay; the average temperature of the seawater is about 24℃ in the summer and about 8℃ in the winter. The test specimens were set up within the scope of L.W.L. ± 0～＋1.3m. The test specimens are not splashed in the pool.

3. Preparation of Test Specimens

(1) Materials Used

Seven types of cement, ordinary portland cement (symbol: N0, N2), high early strength portland cement (H0), moderate heat portland cement (M0), blast furnace slag cement B-class in JIS (B0, B2) and aluminous cement (AL), were used. As for N0, H0, M0 and B0, the three brand-name cements on the market are mixed in equal quantities respectively. In N2 and B2, a quantity of gypsum phosphate of 2% by weight of sulfur trioxide (SO_3) was added to N0 and B0 respectively[8]. AL used was the one commonly found in the market. **Tables 1 to 3** show the chemical composition and physical test results of the cement. The SO_3 quantities of N2 and B2 are higher than the quality standard of JIS R 5210 and 5211.

Table 1 Chemical components of cement

Cement	Ig.loss (%)	Insol. (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	S (%)	F.cao (%)
N 0	0.8	0.3	5.5	3.1	21.7	64.7	1.3	2.0	0.30	0.57	–	0.9
N 2	1.7	0.3	5.2	2.9	20.7	63.3	1.2	3.9	0.27	0.56	–	0.9
H 0	1.1	0.5	5.2	2.7	20.6	65.3	1.2	2.5	0.37	0.54	–	0.9
M 0	0.8	0.2	4.5	3.8	23.5	63.4	1.2	1.7	0.28	0.48	–	0.5
B 0	0.4	0.7	9.7	2.1	25.7	54.1	3.2	2.4	0.46	0.51	0.4	0.3
B 2	1.3	0.6	9.3	2.0	24.4	53.2	3.0	4.3	0.44	0.48	0.4	0.4

Table 2 Physical properties of cement (N0,N2,H0,M0,B0,B2)

Type of cement	Specific gravity	Specific surface area (cm^2/g)	Setting time			Flow (mm)	Compressive strength(kgf/cm^2)		
			W/C (%)	Initial (h-m)	Final (h-m)		3d.	7d.	28d.
N 0	3.14	3180	27.5	2-28	3-28	250	131	226	422
N 2	3.12	3570	27.8	2-50	3-50	249	159	231	380
H 0	3.13	4290	29.0	2-23	3-26	259	226	338	447
M 0	3.19	3260	25.5	3-02	4-27	255	90	146	317
B 0	3.04	3850	28.6	3-34	5-10	255	97	152	346
B 2	3.00	4100	29.0	3-54	5-52	253	95	152	325

Table 3 Physical properties of cement (AL)

Chemical component (%)			Specific gravity	Specific surface area (cm^2/g)	Flexural strength (1day) (kgf/cm^2)	Compressive strength (3days) (kgf/cm^2)
Al_2O_3	Fe_2O_3	CaO				
60.6	2.5	32.5	2.98	4230	67.2	468

Since one of the objectives of the research is the evaluation of the durability of seawater-mixing concrete, tap water (symbol: W) and seawater (symbol: S) were used as mixing water of concrete. The chemical composition of the seawater is shown in **Table 4**. In this paper, hereinafter the kind of concrete is abbreviated by pairing a cement with a mixing water, for example (AL, W).

Table 4 Chemical components of seawater used for concrete mixing

Specific gravity (20℃)	pH (20℃)	Chemical component (mg/l)						
		Na	K	Ca	Mg	Cl	SO_4	CO_3
1.024	8.03	10125	387	376	1180	17136	2412	65

As for coarse aggregate and fine aggregate, river gravel (maximum size: 25 mm) and river sand produced at the Sagami River, Kanagawa Prefecture, were used.

All the concrete was mixed with water reducing agent as admixture; for (AL, W), air entraining agents were also used. As for the reinforcement, ϕ 9mm round bars specified in JIS G 3112 were used in brilliant conditions; the black layer was removed.

(2) Fabrication of Test Specimens

For the test of compressive strength, corrosion of reinforcement and mix potential, cylindrical test specimens (ϕ 15 × 30 cm) were fabricated with the concrete shown in **Table 5**.

As for the test specimens used for the measurement of the corrosion of reinforcement and mix potential, three reinforcements were embedded with a cover depth of 2 cm, 4 cm and 7 cm as shown in **Fig. 1**. Lead wires were soldered to the reinforcement in the test specimens for mix potential measurement.

Table 5 Specified mix proportions of concrete

Cement	Water	Gmax (cm)	Slump (cm)	Air (%)	W/C (%)	s/a (%)	Unit quantity (kg/m³)					
							W	C	S	G	WE (l)	AE (cc)
NO	W	25	66	34	52.7	37.0	153	290	740	1261	2.9	-
	S	25	56	32	53.4	36.0	155	290	718	1277	2.9	-
N2	W	25	64	40	54.5	37.0	158	290	734	1251	2.9	-
	S	25	51	34	55.2	36.0	160	290	713	1270	2.9	-
HO	W	25	37	39	53.1	37.0	154	290	738	1258	2.9	-
	S	25	57	31	55.2	36.0	160	290	711	1263	2.9	-
MO	W	25	65	48	52.4	37.0	152	290	742	1264	2.9	-
	S	25	46	40	53.1	36.0	154	290	720	1280	2.9	-
BO	W	25	35	30	52.4	37.0	152	290	738	1258	2.9	-
	S	25	40	38	53.1	36.0	154	290	716	1274	2.9	-
B2	W	25	42	38	54.8	37.0	159	290	729	1242	2.9	-
	S	25	47	41	55.5	36.0	161	290	708	1258	2.9	-
AL	W	25	63	31	52.1	37.0	151	290	737	1256	2.9	20
	S	25	51	35	52.8	36.0	153	290	716	1272	2.9	-

* Slump and air content are measured values

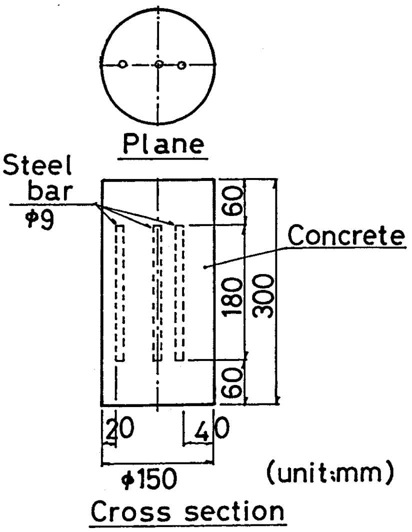


Fig. 1 Dimensions of specimen

The concrete was mixed by 200-liter forced-mixing-type mixers; the mixing and placing were conducted in a 20℃ constant temperature room. Concrete was cast in two layers; each layer was compacted with vibrators.

(3) Curing of the Test Specimens

The casted concrete test specimens were kept in a constant temperature room. At the age of one day, the molds were removed, and moved into a standard curing water tank (water temperature: 21℃) and cured for six days (in the case of HO, they are cured for three days). Then, they were moved into the tidal pool and the exposure test was started. However, in the case of (AL,S), the molds were removed at an age of 4 days, and they were moved into the tidal pool. In the case of (AL, W), the molds were removed at the age of one day, and moved into the tidal pool.

4. Test Method

Main test items are as follows.

a) Compressive Strength of Concrete
The test was carried out according to JIS A 1108 at the initial stage and at the age of one year, 5 years, 10 years and 20 years . The above initial stage means an age of 28 days as a rule; however, the exceptions are as follows: in the case of (AL, W), it means one day, in the case of (AL, S), it means 4 days, and in the case of HO, it means 7 days.

b) X-ray Diffraction Analysis
At the age of 20 years, to confirm the crystal minerals in concrete, X-ray diffraction analysis was performed. The samples tested were taken at two places, 1 cm and 7.5 cm deep from the surface at the center in the longitudinal direction of the concrete test specimens. They were crushed into powder.

c) Carbonation Depth of Concrete
Carbonation depth of concrete was measured with the phenolphthalein method at the age of one, 5, 10 and 20 years.

d) Corrosion of the Reinforcement in Concrete
Measurements of corrosion of reinforcement were performed on three to five specimens of reinforcement at every covering depth at 5, 10 and 20 years.

As for the reinforcement removed out from the concrete test specimens, visible rust was traced and the corroded area was measured with planimeters. From the results, the rate of corrosion for the surface area of reinforcement was calculated.

e) Mix Potential of the Reinforcement in Concrete
The mix potential of reinforcement was measured for the same test specimens in January, April, July and October annually, up to 20 years after the start of the exposure test. The measurements were performed by immersing the test specimens in the seawater completely. Seawater silver chloride electrodes were used as

reference electrodes.

f) Anodic Polarization of Reinforcement in Concrete
The anodic polarization of reinforcement was performed for each mix and each cover at 10, 15 and 20-years. The concrete at the top of the test specimens were removed by chipping, and lead wires were connected to the exposed reinforcement and covered with epoxy resin. The measurements were performed by immersing the test specimens in the seawater. As for a reference and a counter electrode, a saturated calomel electrode and a stainless steel plate were used respectively.

From the shape of the anodic polarization curve, the conditions of the passivity of the reinforcement were classified as grade-0 (poor passivity) to grade-5 (good passivity) [9].

g) Chloride Content in Concrete
Chloride content in concrete was tested at 10, 15 and 20 years. The five to 10 g of concrete near each reinforcement (depth: 2 cm, 4 cm, 7 cm) of the test specimens was sampled and the coarse aggregate was removed; the rest was pulverized under 105 μ m. Water-soluble chloride ions from these samples were extracted with the 24-hour extraction method at 20℃ using distilled water [9], and quantitative analysis was performed according to the silver chromate-absorptiometric method [10].

h) Diffusion Coefficient of Oxygen in Concrete
The diffusion coefficient of oxygen in concrete was surveyed by the Japan Concrete Institute method [11] for each mixture at 20 years of aging. As for the test specimens, 2 cm thicknesses between 3 and 5 cm from the top and bottom of concrete test specimens were used as test specimens. The diffusion coefficient was measured when the ratio of water saturation was 0, 60 and 80%.

5. Test Results and Discussion

(1) Strength Characteristics of Concrete

a) Surface Appearance of Concrete
The surface appearance of concrete were observed at 5, 10 and 20 years; at 5 and 10 years, only stains and rough surfaces were recognized, while at 20 years, cracks and spalling were recognized in some test specimens. Many fine cracks and spalling were recognized on the surface of most test specimens of portland cement, while they were not recognized on the surface of the test specimens of blast furnace slag cement and aluminous cement.

The main cause for the cracks and spalling development is considered to be the expansibility of ettringite . The details are described in c) with respect to the reason for decrease in strength.

The difference in cracks and spalling caused by the difference between tap water and seawater was not recognized.

b) Compressive Strength of Concrete

Figure 2 shows the time-dependent change of the compressive strength f'_c of seawater mix concrete. **Figure 3** shows the time-dependent change in the strength ratio (hereinafter, called initial strength ratio), which divides the strength at each stage by the initial strength f'_{co} of each mixture. **Figure 4** shows the change of the initial strength ratio of tap water mix concrete. As for the relation between the aging and strength, it increases up to 5 years in most test specimens; however, after 5 years of aging the strength has a tendency to fall gradually and at the age of 20 years the strength is less than the initial strength. Such a tendency for concrete exposed to seawater has been reported often [3], [12],[13].

The initial strength ratio at the age of 20 years was 0.76 to 0.94 in the portland cement group, 0.98 to 1.01 in the blast furnace slag cement group, and 0.79 in aluminous cement. The initial strength ratio of the blast furnace slag cement was relatively high; this means that the strength loss is less than in other cements.

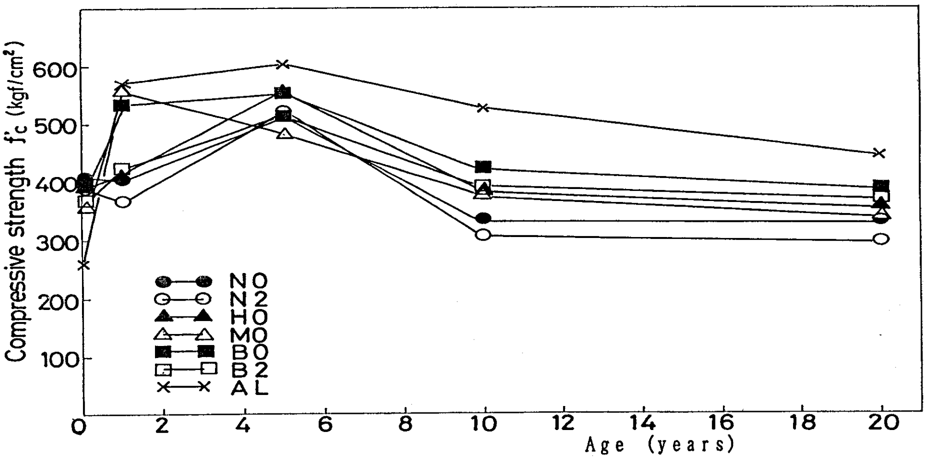
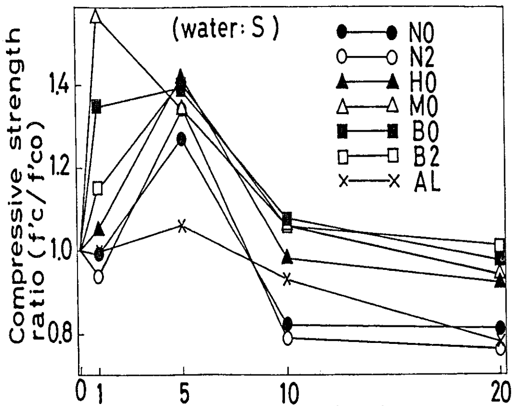


Fig. 2 Strength of concrete mixed with seawater



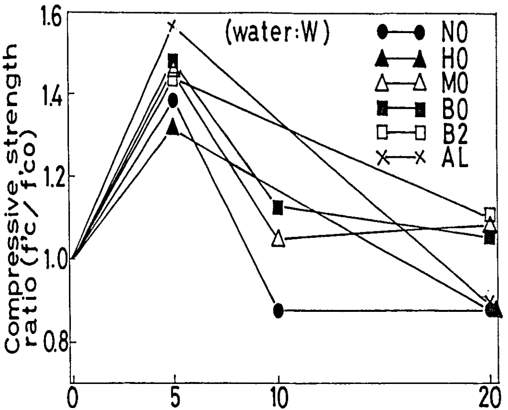


Fig. 3 Compressive strength ratio f'_c/f'_{co} (mixed with tap water)

Fig. 4 Compressive strength ratio f'_c/f'_{co} (mixed with tap water)

Figure 5 shows the time-dependent change of the compressive strength ratio (hereinafter, called the seawater/tap-water strength ratio) using seawater and tap water as mix water. Since concrete using seawater has slightly more strength in the early stage than that using tap water, the compressive strength ratio of most test specimens at 28 day aging was more than 1.0. However, later, the compressive strength ratio approaches 1.0, and at 20 years of aging it became 0.92 to 1.03. Thus, since the seawater/tap-water strength ratio of the portland cement and blast furnace slag cement group became approximately 1.0 at an advanced age, it is considered that the use of seawater for mixing is independent of the compressive strength of the long-term aging of concrete. This was also reported by Gjorv[3].

Aluminous cement shows a very unique tendency compared to the portland cement and blast furnace slag cement group. The delay of the development of strength of (AL, S) is assumed to be caused by the formation of aluminate chloride; this phenomenon has been demonstrated [14],[15], and it will be discussed in d) that the seawater/tap-water strength ratio at 20 years exceeds 1.0 markedly. It is supposed that gypsum in cement does not have an effect on the strength of concrete.

c) Cause of the Decrease in Strength of the Concrete with Portand Cement and Blast Furnace Slag Cement Group

It is said that in the portland cement and blast furnace slag cement group, at a relatively early age in seawater, chloride ions which penetrate into concrete react with calcium hydroxide, and then the concrete is made porous causing decrease in strength [16]. While at an advanced age, C_3A in concrete reacts with sulphuric acid ion in seawater and ettringite is generated, it is said that the expansion failure of the surface of the concrete causes decrease in strength.

Table 6 shows the results of the X-ray diffraction analysis of the concrete at 20 years of aging. From **Table 6**, the following may be said.

① The ettringite was recognized in all samples; there is hardly a difference among the quantities generated using different types of cement and water.

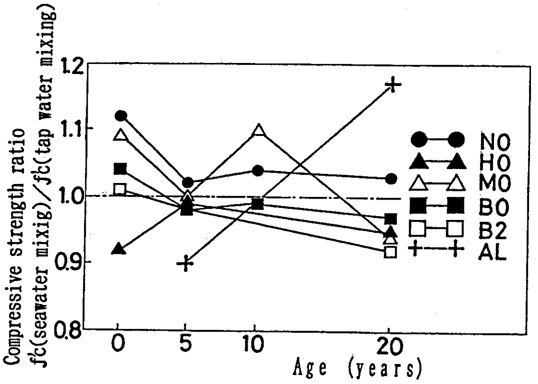


Fig. 5 Compressive strength ratio (mixed with seawater v.s tap water)

Table 6 X-ray analysis(N0,N2,H0,M0,B0,B2)

Cement	Water	(cm)	Ettringite	Friedel's salt	$CaCO_3$	$Ca(OH)_2$
NO	W	1	+	++	+	
		3	+	++	+	
		5	+	++	+	
		7.5	+	++	+	
	S	1	+	++	+	
		7.5	+	++	+	+
N2	W	1	+	++	+	
		7.5	+	++	+	
	S	1	+	++	+	
		7.5	+	+		+
HO	W	1	+	++	+	
		7.5	+	++	++	
	S	1	+	++	+	
		7.5	+	++	+	+
MO	W	1	+	++	+	
		7.5	+	+	+	
	S	1	+	++	+	
		7.5	+	++	+	+
BO	W	1	+	++	+	
		3	+	+	++	
		5	+	+	+	+
		7.5	+		+	+
	S	1	+	++	+	
		7.5	+	+	+	+
B2	W	1	+	++	+	
		7.5	+		+	+
	S	1	+	+	+	
		7.5	+	+	+	+

\+ : CPS (counts per second) is less than 500
++ : CPS (counts per second) ranges from 500 to 2000

② Friedel's salt was recognized in most samples. However, it was not detected in the center of the tap water mix concrete using blast furnace slag cement. It may be suggested that the penetrating speed of chloride ions in this mixture is slow [17].

③ Calcium hydroxide was not detected on the surface of all the test specimens; particularly in the portland cement and tap water mix concrete, calcium hydroxide was not detected even in the center of the test specimens. It was found that in the blast furnace slag cement group concrete or seawater mix concrete, calcium hydroxide remains near the center of the test specimens.
These results suggest the following: the elusion of calcium hydroxide from the concrete surface can be reduced by using the blast furnace slag cement or seawater mix concrete, but it cannot be avoided under a marine environment over 20 years.

④ Calcium carbonate generated by the reaction of calcium hydroxide on carbon dioxide was recognized in all samples.
From the above results, the decrease in strength of the portland cement and blast furnace slag cement group under marine environment, particularly the portland cement group, is assumed to be caused by the expansion due to generated ettringite formation. From the results of the X-ray diffraction test, there is no indication that seawater mix concrete is less durable than tap water mix concrete.

d) Strength of Concrete used Aluminous Cement
As for aluminous cement, CA, which is the main chemical component, reacts with water, and converts into stable C_3AH_6 and $2AH_3$ through a semistable compound such as CAH_{10}. It is said that the conversion makes the organization of the hydration hardening body porous, and increases in void cause the release of the water of crystallization resulting in decrease in strength.

Table 7 shows the generative minerals confirmed by X-ray diffraction in the samples using aluminous cement in the same way as c); in the concrete, C_3AH_6 and $2AH_3$ were recognized. From this, it was confirmed that the conversion from CAH_{10} into C_3AH_6 and $2AH_3$ caused the decrease in strength of concrete. Meanwhile, in the comparison of the outer layer of concrete with the center, CAH_{10} remains to a smaller degree in the center of the tap water mix concrete, while there is no sign of C_3AH_6 in the outer layer, and much was recognized in the center of the tap water mix concrete. Similarly, there is also no sign of $2AH_3$ in the outer layer, while much was recognized in the center.

Table 7 X-ray analysis(AL)

Mixing water	Sampling depth (cm)	CAH_{10}	C_3AH_6	$2AH_3$
W	1.0	++		+
	7.5	+	++	++
S	1.0	++		+
	7.5	++	+	++

\+ : CPS (counts per second) is less than 500
++ : CPS (counts per second) ranges from 500 to 2000

Eventually, much CAH_{10} remains in the outer layer which is greatly affected by seawater and in the seawater mix concrete; this indicates that there is a small quantity of conversion to C_3AH_6 or $2AH_3$.

From these results, seawater as mix water contributes to reduce the conversion and to inhibit the decrease of long-term strength though seawater causes retardation of hardening and setting of aluminous cement at the initial stage of hydration. The results indicate the tendency as shown in **Fig. 5.**

(2) Carbonation Rate of Concrete

Figure 6 shows the relation between the average value x of the maximum carbonation depth at the cross section of the concrete test specimens and age t, and a value of the approximate expression of $x = a\sqrt{t}$. Though a small difference in the carbonation depth caused by the difference of the types of cement was recognized, there was no effect from mixing water. It is said that the carbonation rates of concrete in the air are 0.79 of high early strength portland cement and 1.41 of blast furnace slag cement B-class when ordinary portland cement is 1.0 [18]. In this research, the same tendency was recognized.

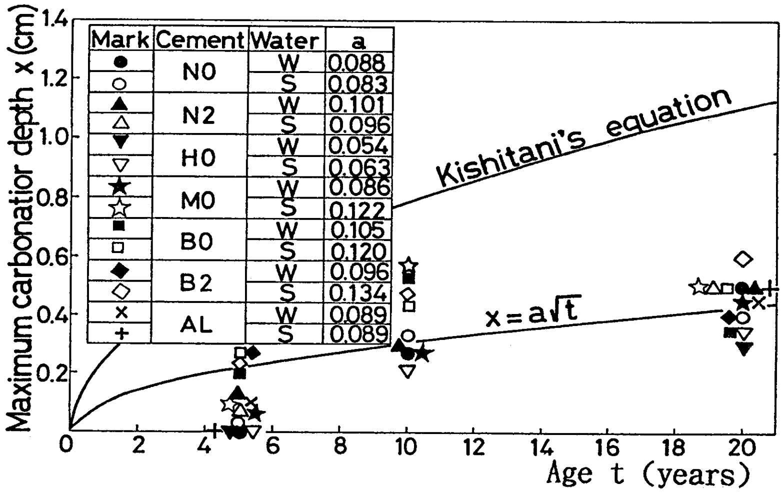


Fig. 6 Depth of carbonation

In **Fig. 6**, the calculation curve for concrete in the air obtained using Kishitani's formula [19] is shown, in which the carbonation ratio R is 1 and water cement ratio is 52.7%. The carbonation rate at the tidal zone obtained by these tests is much smaller than that in the air; according to the approximate expression, its value is equivalent to about 40% of that in the air. By the approximate expression, the maximum carbonation depth at 50 years of aging is about 0.7 cm.

(3) Corrosion Condition of Reinforcements in the Concrete

a) Corroded Area

Figure 7 shows the ratio of corroded area of reinforcements. Each value is the mean value of the measured values of three to five specimens of reinforcement under the same conditions. When measuring the corroded area, rust was classified into black rust and red rust. Black rust is considered to contain a great deal of Fe_3O_4, while red rust is considered to contain a great deal of FeOOH. However, no correlation between differences in rust color and depth of corrosion was found. Furthermore at 20 years of aging a thin black layer in which there were no sectional defects was found. Its area was included in the black coloured rust area at 20 years of aging in the figure.

As shown in the figure, regardless of the type of cement, the corroded area at the ages of 5 and 10 years was very low. The corroded area of blast furnace slag cement and aluminous cement at 20 years of aging was low, while that of portland cement was high. The reason is that the black layer mentioned above was included.

Though the amount of red rust in the seawater mix portland cement at 20 years was a little greater than that of tap water mix concrete, it can be considered that there was no effect of mixing water on the amount of corrosion of reinforcement. Based on this, there seems to be little difference between the seawater mix concrete and tap water mix concrete in their effect on corrosion of reinforcement, at least in the tidal zone.

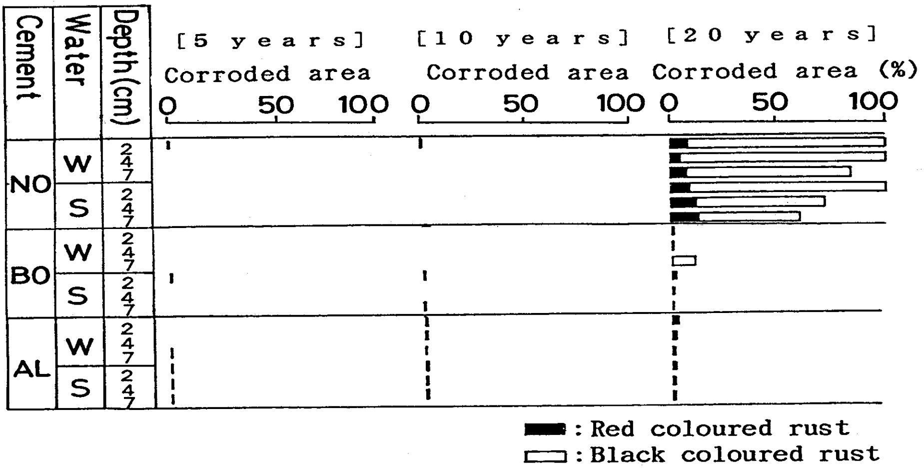


Fig. 7 Corroded area of steel bars

On the other hand, the effect of the type of cement was significant; this effect was particularly obvious at 20 years of aging. As for the corroded area ratio of the reinforcements for the concrete using portland group cement, large amounts of red and black rust were recognized. Meanwhile, blast furnace slag cement was confirmed to be excellent in corrosion prevention. In aluminous cement which is weak in alkalinity and is susceptible to corrosion of reinforcement, there was almost no recognizable rust [20]. Also, the corrosion of reinforcement seems to be slightly affected by an increase in quantity of gypsum in the cement.

As for the effect of cover thickness, the reinforcement using portland cement was affected slightly at 20 years of aging; however, this effect was much smaller than that due to the type of cement.

From the ratio of corroded area of the reinforcements in the concrete, the following results were obtained.

- Rust generation was observed in the reinforcements in concrete using the portland cement at about 20 years of aging even with a covering of 7 cm.
- The blast furnace slag cement and aluminous cement were more resistant to the corrosion of reinforcement than portland cement.
- Differences in the type of cement had a large effect on the corroded area.

- The use of seawater as the mixing water did not affect the corroded area very much.
- The effect of differences in covering thickness less than 7 cm on the corroded area was smaller than that of the differences in the type of cement.

b)Judgment of the grade of passivity

The results of the grade of passivity of the reinforcements, as judged from the anodic polarization curve, are presented in **Table 8**. From the table, it can be seen that as in the tendencies of the corroded area, the effect of the type of cement was more significant than that of the mixing water or covering depth. That is, the grade of passivity of the reinforcements in the concrete which used the blast furnace slag cement or aluminous cement was superior to that of the portland cement. Clearly, this corresponds to the small value of corroded area in the concrete which used blast furnace slag group cement or aluminous cement.

Table 8 Grade of passivity

Cement	Water	Depth (cm)	Grade of Passivity	
			15 years	20 years
NO	W	2	2	2
		4	2	2
		7	2	2
	S	2	1	2
		4	2	2
		7	2	2
MO	W	2	2	2
		4	2	2
		7	2	2
	S	2	2	2
		4	2	2
		7	2	2
BO	W	2	4	4
		4	4	5
		7	4	5
	S	2	4	4
		4	4	5
		7	4	5
AL	W	2		5
		4		5
		7		5
	S	2		5
		4		5
		7		5

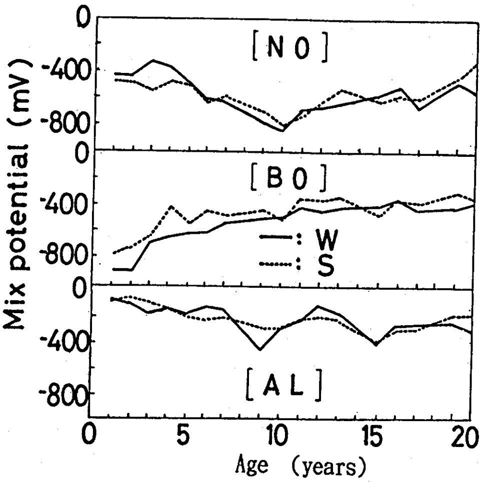


Fig. 8 Change of mix potential

c)Time-dependent change in mix potential with time

A typical change in mix potential with time is shown in **Fig. 8.** The value for each year is an average of the measured values for the three test specimens in January, April, July and October of the measuring period.
In short-term aging, there was a small difference between the values for seawater mix and those for tap water mix, but in long-term aging the values for seawater mix were the same as those for tap water mix.

The tendencies of the change in mix potential depended on the type of cement used. As for the mix potential of the reinforcements in the test specimens which used NO, the potential had a tendency to move to the base side up to 10-years of aging and to move to the noble side after that. As for those which used BO, the potential had a tendency to gradually move to the noble side up to 20-years of aging. Moreover, as for those which used AL, the potential had a tendency to move to the base side up to 20 years of aging.

The tendencies of the changes in the potential to differ depending on the type of cement used are considered to be mainly caused by differences in the oxygen content around the reinforcement. The corrosion reaction is expressed by the following formulas, (1) and (2), and the anode reaction (1) and cathode reaction (2) progress equivalently.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1)$$

$$1/2O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad (2)$$

The mix potential is interpreted to be the potential at the intersection of the anodic and cathodic polarization curves. Since the cathodic reaction is controlled by oxygen, as shown in formula (2), the cathodic polarization curve is changed by the quantity of oxygen around the reinforcement; even in the case where the anodic polarization curve is constant, the mix potential is changed.

Figure 9 shows imaginary anodic and cathodic polarization curves for objects using NO, BO and AL. In the anodic polarization curve, since the reinforcements have good passivity at the initial age, this is expressed as Ao in the figure. However, this is thought to change to A1 and A2 due to the effect of salt, after the passage of 10 years to 20 years of aging. Also, as is shown in b), where the grade of passivity of the reinforcements depends on the type of cement, the anodic polarization curve also depends on the type of cement. On the other hand, though the cathodic polarization curve is Co at the initial aging, the oxygen density rises with the progress of aging, and it is thought to change to C1 and C2. Also, the quantity of oxygen around the reinforcement depends on the type of cement. If the magnitude of the oxygen diffusion is largest for AL followed by NO and BO in that order, the cathodic polarization also depends on the type of cement, as shown in the figure. Therefore, it can be considered that the mix potential Eo, E1 and E2, which changes with the passage of time, also depends on the type of cement. The experimental results of diffusion of oxygen are shown in (4) c).

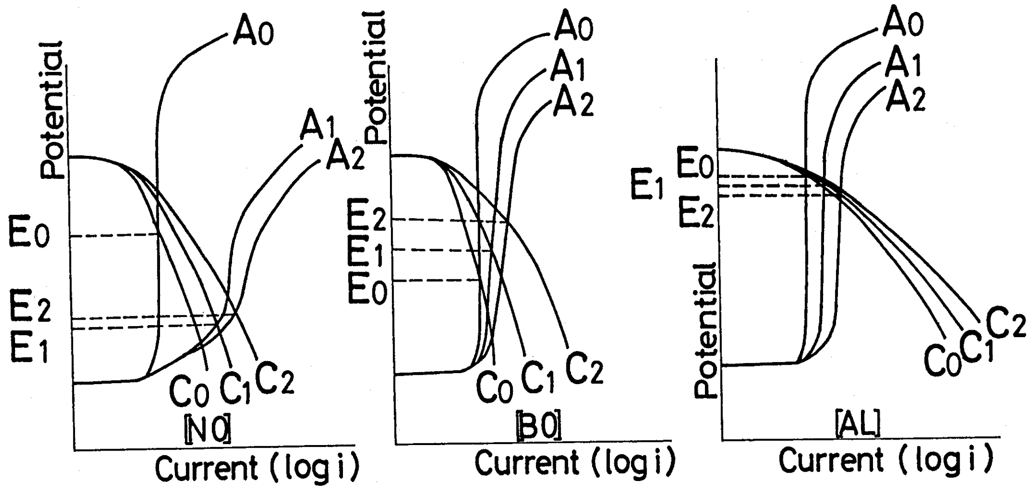


Fig. 9 Assumed polarization curves of steel bars

(4)Chloride Ions and Oxygen in the Concrete

a)Chloride Ion Content in the Concrete

Figure 10 shows the water-soluble chloride ion as a weight percentage for mortar. In the mix conditions used here, concrete mixed with seawater contained chloride ions of 0.22 to 0.24% (2.59 to 2.76 kg per $1m^3$ concrete) of the mortar weight in the fresh concrete state. This value is more than four times 0.6 kg/m^3 which is considered as the allowable chloride content in fresh concrete. As shown in **Fig.10**, in the concrete which used ordinary portland cement, the chloride content averaged 1.4% at 10 years of aging, 1.75% at 15 years of aging and 2.0% at 20 years of aging. When comparing these values with that of the fresh concrete, these values are 6.1, 7.6 and 8.7 times greater, respectively. Furthermore, in NO, since there is little increase in the chloride content between 10 and 20 years of aging, the chloride ions in the concrete are thought to nearly reach a condition of saturation at around 10 years of aging.

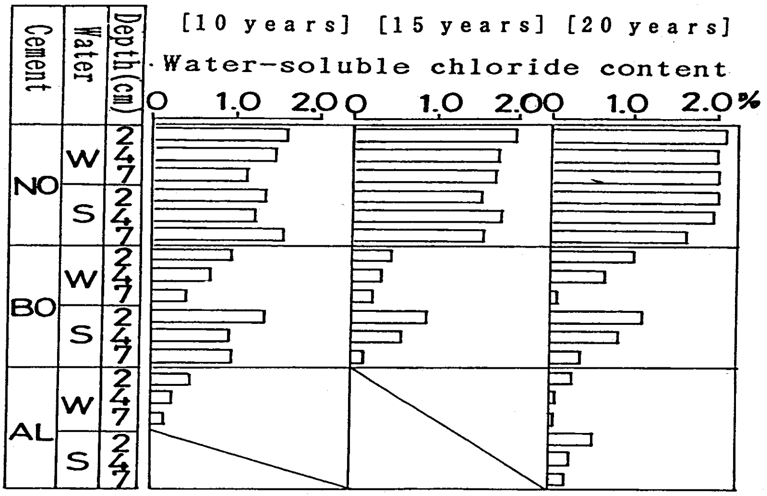


Fig. 10 Water-soluble chloride content in concrete

On the other hand, the chloride content in BO and AL was much lower than that in NO, and the chloride ion content at the age of 20 years was only 30% of that of NO on the average. It is said that BO is strongly resistant to the penetration of chloride ions due to their minute composition [17]; this was confirmed by this research.

As for the effect of the use of seawater as the mixing water on the chloride ion content in the concrete, no effect was seen with NO; however, BO and AL were affected slightly because the amount of chloride penetration from the seawater is small. However, this effect was much smaller than that of cement type.

As for the effect of cover thickness on chloride ion quantity, there was no effect with NO, the same as with the case of mix water. In contrast with BO and AL, the effect of the cover thickness was marked; if a sufficient cover depth is used a cover can prevent the penetration of salt.

From these results, the following points became clear:

In the case where seawater acts on concrete for a long time, the resistance of portland cement to the penetration of salt is lower than that of blast furnace slag cement or aluminous cement; salt is more apt to penetrate into portland cement than into the other cements. It was also found that the use of seawater as mixing water had little effect on the chloride ion content in the mortar.

b)Relationship between Chloride Content and the Corroded Area of Reinforcement

Figure 11 shows the relationship between the water-soluble chloride content around the reinforcements and the corroded area. Since the corrosion reaction progresses in a complicated relationship with factors such as oxygen supply and moisture in addition to chloride content, the relationship between chloride content and corroded area is not determined unconditionally. However, as shown in **Fig. 11**, when the water-soluble chloride content exceeds 1.5% in mortar weight, there was a clear tendency towards an increase in the corroded area.

c) Diffusion Coefficient of Oxygen

Measured results of the diffusion coefficient of oxygen, which controls the cathodic reaction, are shown in **Fig. 12**. Each value is an average value of samples taken from the top and bottom of the test specimens.

As shown in the figure, mixing water had no recognizable effect on the diffusion coefficient of oxygen, but there were recognizable effects of the type of cement. The average diffusion coefficients for each type of cement in the case of saturation of 0% were as follows:

portland cement	:	9.35×10^{-4} to 10.57×10^{-4} cm^2/s
blast furnace slag cement	:	6.99×10^{-4} to 9.06×10^{-4} cm^2/s
aluminous cement	:	26.80×10^{-4} cm^2/s

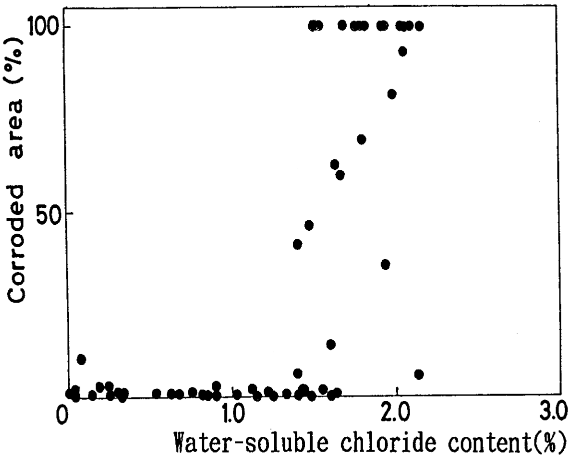


Fig. 11 Relationship between chloride content in concrete and corroded area of steel bars

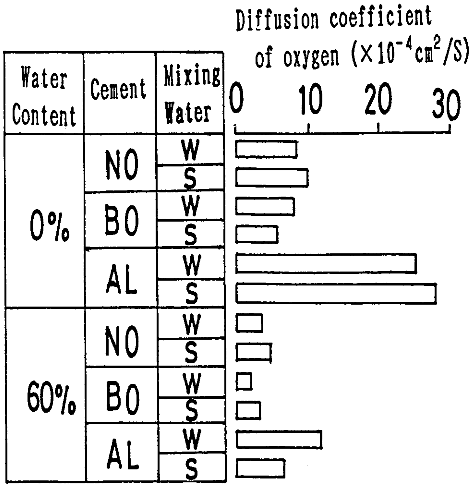


Fig. 12 Diffusion coefficient of oxygen of concrete

The average diffusion coefficient for blast furnace slag cement was slightly lower than that for portland cement. In contrast, that for aluminous cement was markedly higher. This can be explained by high porosity due to the conversion of mortal of aluminous cement. Also, in the case of water saturation of 60%, the diffusion coefficient becomes smaller than that of saturation of 0%, but the effects of the type of cement showed the same tendencies. This supports the ideas relating to the cathodic polarization curve mentioned in (3) c).

In the case of aluminous cement, despite the fact that the amount of penetrated chloride ions was small, the diffusion coefficient of oxygen was large. The following reason for this can be considered. According to the results of X-ray diffraction of the test specimens which used aluminous cement, it was seen that the degree of porosity caused by the conversion of CAH10 into C3AH6 at the surface was less than that at the center. The chloride ions penetrate from the surface of the test specimens, but the amount of penetrated chloride ions was small, since at the surface the degree of porosity was low. On the other hand, since the location where the diffusion test was performed was at the center of the test specimens, a location which had become porous, a large diffusion coefficient was obtained.

6. Conclusions

The results of the exposure test for a 20 year period under a marine environment (tidal zone) can be summarized as follows.

(1) In the concrete using portland cement, such as ordinary, high early strength and moderate heat types, there were many recognizable fine cracks and fine spalling on the surface at the age of 20 years. On the other hand, less cracks and spalling were found on the surface of the concretes using blast furnace slag cement B-class and aluminous cement.

(2) The compressive strength of concrete increases up to about 5 years of aging; after this it gradually decreases. At 20 years of aging most specimens had a tendency to be below their initial strength. There were no differences in compressive strength due to differences in mixing water with long-term aging.

(3) Based on the corroded area and the grade of passivity, it was clear that the corrosion of the reinforcements in the concrete using portland cement progresses up to 20 years of aging. Corrosion is significantly affected by the type of cement used; it was seen that the corrosion with the concrete using blast furnace slag cement or aluminous cement was less than with that using portland cement. It was clear that there was almost no recognizable effect on the corrosion of reinforcements due to differences in mixing water.

(4) As for preventing the penetration of salt, the concrete using blast furnace slag cement and aluminous cement was much better than that using portland cement. There was a small recognizable effect of the mixing water on the chloride ion content in the concrete using blast furnace slag cement B-class and aluminous cement at 20 years of aging, but there was no effect on the concrete using portland cement.

(5) There was no effect of mixing water on the diffusion coefficient of oxygen in the concrete. On the other hand, there was a recognizable effect of the type of cement used on the diffusion coefficient; the concrete with the lowest diffusion coefficient was blast furnace slag cement, while that with the highest coefficient was aluminous cement.

(6) Within the scope of this study, even when gypsum phosphate with 2% in SO_3 weight was added to ordinary portland cement and blast furnace slag cement B-class, there was no recognizable effect on the durability of the concrete.

(7) In this 20-years series of experiments, concrete using blast furnace slag cement and aluminous cement shows excellent performance against seawater attack and corrosion of reinforcement. Furthermore, it was found that seawater as mixing water of concrete has little effect on the durability of concrete and corrosion of reinforcement, when concrete has been exposed in the tidal zone for a long time.

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